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Harold Johnston and Richard Graham

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Gas Phase Ultraviolet Absorption Spectrum of Nitric Acid Vapor

Harold Johnston and Richard Graham

Department of Chemistry
University of California
and Inorganic Materials Research Division,
Lawrence Berkeley Laboratory,
Berkeley, Calfiornia 94720

Abstract

The absorption cross section for nitric acid vapor has been determined between 190 and 325 nm at room temperature. The results agree with work by Dalmon over a shorter wave-length interval. The nitric acid spectrum is a continuum, consists of at least two different electronic states, and obeys Beer's law throughout the region. The absorption cross section is above 10^{-17} cm^2 at 190 nm, about 10^{-20} cm^2 between 240 and 290 nm, and less than 10^{-22} cm^2 from 322 to 370 nm, which is the upper wave-length range of this study.

Nitric acid vapor is an important by-product of photochemical smog[1], and it is an important trace constituent in the lower stratosphere.[2] For photochemical smog, the interesting wave length region for the absorption coefficient and quantum yields is that above 300 nm. For the stratosphere, the entire wave length region above 190 nm is interesting. This article gives the absorption spectrum from 190 to 370 nm. Work is in progress concerning the quantum yields and the identity of the primary products of the photolysis processes.

EXPERIMENTAL

The observations were made with a McPherson 0.3 meter scanning monochromator in conjunction with a multiple reflection long-path gas cell. The 45 liter cell consisted of a 6-foot long quartz tube, 6 inches in diameter, and nickel-plated stainless-steel end caps. External lines were glass or stainless steel. The base path of the cell is 8.6 m, and optical paths of 8.6 to 34.4 m were used. A slit-width of 0.5 mm gave 0.7 nm resolution. The source lamp was a Sylvania deuterium arc, and a set of mirrors mounted near the cell entrance and exit windows diverted part of the light as a reference beam. A filter was used above 370 nm to remove light diffracted in second order. The source beam was chopped at 400 cps and detected with a photomultiplier and a lock-in amplifier. Scans were recorded and evaluated by a PDP 8/L computer interfaced with a Fabritek 1074 computer.

Pure nitric acid was prepared from a mixture of dry sodium nitrate and 98.5% sulfuric acid. The distilling bulb was filled at dry-ice temperature, then evacuated and warmed to 40°C; the collecting vessel for the nitric acid was placed in a -40°C bath (These temperature limits should not be exceeded, or nitric acid will decompose above 40°C). The product was stored as a white solid at dry-ice temperature. Westef greaseless Teflon and Viton o-ring stopcocks were used. Gas samples were collected in either an 80 cc bulb or a 3-liter bulb, and the pressure was measured with an oil manometer. The gas was then expanded into the evacuated gas cell and scans were made within 10 minutes.

Nitrogen dioxide gas of 99.5% purity from Matheson Company was liquified and stored for 48 hours at 0°C with one atmosphere of oxygen. The NO_2 was then frozen at dry-ice temperature and the oxygen was pumped off. The solid was transferred twice and pumped on to remove any trapped oxygen. The white product was stored at dry-ice temperature. Nitrogen dioxide samples were collected in an 80 cc. bulb at 25°C, and the pressure was measured with an oil manometer. Corrections for N_2O_4 were made using the equilibrium constant of Verhoek and Daniels.[3] The gas samples were then expanded into the evacuated cell. The absorption spectrum is based on ten gas samples which gave cell concentrations between 5×10^{14} molecules/cm^3 and 3×10^{15} molecules/cm^3. The maximum amount of N_2O_4 present under these conditions was less than 0.1% of the NO_2 present. Beer's law was obeyed and no pressure dependence was observed between 50 microns and one atmosphere total pressure. The absorption spectrum so obtained had a 1% standard deviation above 300 nm. Values of the detailed absorption cross-sections of nitrogen dioxide were stored in the computer and used to correct the observed nitric acid spectrum for the nitrogen dioxide impurity. The amount of nitrogen dioxide was determined from its detailed spectrum between 310 and 370 nm, and it was found to be between 0.1 and 0.2% of the HNO_3. The absorption due to this source was subtracted from the HNO_3 spectra.

Fifteen gas samples of nitric acid were used and gave cell concentrations between 8×10^{13} and 6×10^{16} molecules cm^{-3}. The composite spectrum is presented on a semilogarithmic plot in Figure 1. The ordinate is in cm^2 $molecule^{-1}$ and the standard deviation is expressed as per cent at the top of the figure. The absorption is very strong between 190 and 210 nm, falls to much lower values between 230 and 290 nm, and rapidly falls to a vanishingly low value above 325 nm.

DISCUSSION

The absorption spectrum of nitric acid in Figure 1 indicates two or more electronic states. To effect some separation of overlapping absorptions, it was assumed that the long-wave-length absorption was symmetrical in energy, centered at 260 nm. This curve is indicated by a dashed line in Figure 1, and it was subtracted from the total absorption curve to give the other dashed line. According to this analysis the short-wave-length absorption has its origin near 280 nm.

The continuous nature of the absorption spectrum suggests that photodissociation is taking place. Four energetically possible reactions are:

A. $HNO_3 + h\nu \rightarrow HO + NO_2$ $\lambda \leq 598$ nm

B. $HNO_3 + h\nu \rightarrow HNO_2 + O(^3P)$ $\lambda \leq 401$ nm

C. $HNO_3 + h\nu \rightarrow H + NO_3$ $\lambda \leq 290$ nm

D. $HNO_3 + h\nu \rightarrow HNO_2 + O(^1D)$ $\lambda \leq 245$ nm

These wave-length limits are derived from thermodynamic data.[4]

This study agrees rather well with that of Dalmon[5] between 230 and 300 nm. The comparison is given in Table 1. The disagreement at 290 and 300 nm could be due to Dalmon's having 1.5% NO_2 in his nitric acid.

For considerations of photochemical air pollution in the troposphere, the important region is that above 300 nm. The observed curve in this region is extremely sensitive to traces of nitrogen dioxide as impurity in the nitric acid and to the completeness with which corrections can be applied for such nitrogen dioxide and for the nitrogen tetroxide in equilibrium with it. In this study the nitrogen dioxide was kept below 0.2% and the nitrogen tetroxide was negligible, about 10^{-10} atm. To provide a firm basis for correcting for the 0.1 to 0.2% NO_2 in our sample, we determined the NO_2 absorption cross section at low pressures and with a long optical path. The absorption cross sections agree with those of Hall and Blacet[6] between 370 and 420 nm and are somewhat lower at shorter wavelengths (as well as the points can be read off of their graph). The cross sections for NO_2 between 200 and 270 nm agreed with those of Nakayama, Kitamura, and Watanabe[7] within their experiemntal error of 30%.

The reproducibility and sensitivity of the apparatus are such that between 330 and 370 nm

$$\sigma(HNO_3) \ll 10^{-22}\ cm^2$$

Furthermore, pure anhydrous nitric acid in the vapor or in the liquid state is clear and colorless, which implies no significant absorptions between 400 and 700 nm. We disagree with the strong absorption indicated for nitric acid vapor between 320 and 440 nm by Schmidt et al[8], and we suggest that they have present some major impurity or an instrumental malfunction.

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Table 1. Ultraviolet absorption spectrum for nitric acid vapor

λ nm	σ, cm^2 Dalmon	σ, cm^2 This work	Standard deviation %
190		1.32 (-17)*	3
195		9.1 (-18)	3
200		5.5 (-18)	3
205		2.55 (-18)	3
210		9.7 (-19)	3
215		3.28 (-19)	3
220		1.44 (-19)	3
225		8.51 (-20)	1
230	5.35 (-20)*	5.63 (-20)	1
235	3.59 (-20)	3.74 (-20)	1
240	2.56 (-20)	2.60 (-20)	1
245	2.10 (-20)	2.10 (-20)	1
250	1.93 (-20)	1.95 (-20)	1
255	1.91 (-20)	1.94 (-20)	1
260	1.93 (-20)	1.90 (-20)	1
265	1.91 (-20)	1.80 (-20)	1
270	1.64 (-20)	1.63 (-20)	1
275	1.34 (-20)	1.40 (-20)	1
280	1.07 (-20)	1.14 (-20)	1
285	8.79 (-21)	8.77 (-21)	1
290	7.26 (-21)	6.34 (-21)	1
295	5.73 (-21)	4.26 (-21)	5
300	4.59 (-21)	2.76 (-21)	5
305		1.68 (-21)	5
310		9.5 (-22)	5
315		4.7 (-22)	5
320		1.8 (-22)	5
325		2 (-23)	>10

* 5.35 (-20) means 5.35×10^{-20}; $\ell n(I_o/I) = \sigma[HNO_3]L$

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Title to Figure 1. The ultraviolet absorption spectrum of nitric acid vapor; $\ell n(I_o/I) = \sigma[HNO_3]L$, where $[HNO_3]$ is in molecules cm^{-3} and L is optical path in cm. The percentages at the top of the figure refer to the standard deviation based on 15 gas samples.

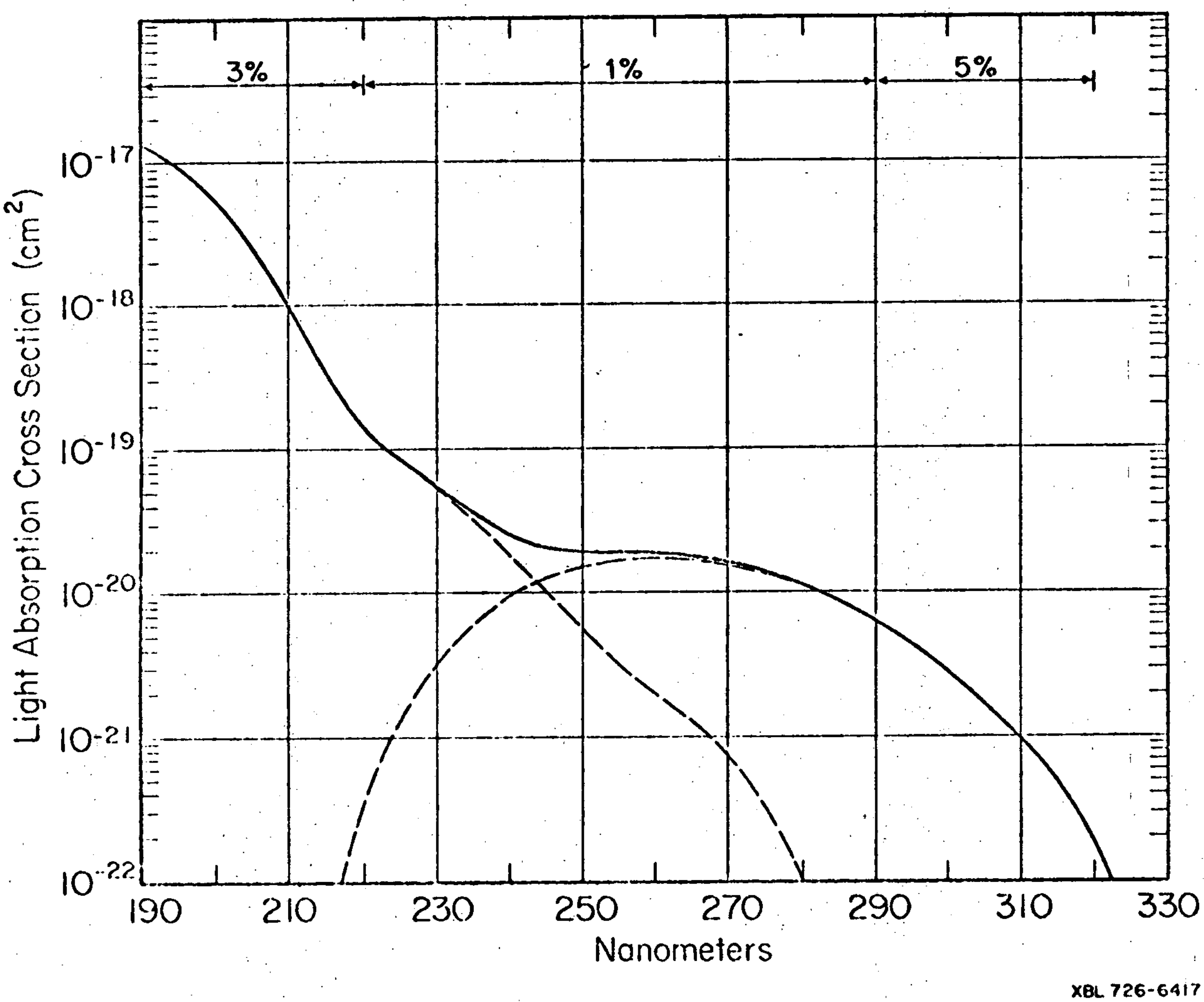
3%
1%
5%
10^{-17}
10^{-18}
10^{-19}
10^{-20}
10^{-21}
10^{-22}
Light Absorption Cross Section (cm^2)
190
210
230
250
270
290
310
330
Nanometers
XBL 726-6417

Fig. 1

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720